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Background Document for Solvents to Support 40 CFR Part 268, Land Disposal Restrictions. Volume 1

Pope-Reid Associates, Inc., St. Paul, MN

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16. Abstract (Limit: 200 words) On November 7, 1986 EPA finalized the regulatory framework for implementing the land disposal restrictions and promulgated treatment standards and associated effective dates for certain spent solvent and dioxin-containing hazardous wastes. The spent halogenated and non-halogenated solvent wastes subject to this final rule are identified by EPA Hazardous Waste no. F001, F002, F003, F004, and F005. This document (Volume I) provides background information regarding production and use of the restricted solvents, and a discussion of physical and chemical characteristics of F001-F005 solvents that are important with respect to the land disposal restriction regulations and their effects on land disposal. Also included are summaries of the toxicity of each of the F001 through F005 solvents, and a description of incidents in which environmental contamination has occurred due to volatilization or migration of solvents.

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SECTION I

BACKGROUND

RCRA Spent Solvent Listings

On May 19, 1980, the Environmental Protection Agency (EPA) promulgated the first phase of the hazardous waste regulations under the Resource Conservation and Recovery Act (RCRA) of 1976, as amended. As part of Section 3001 of RCRA, concerning the Identification and Listing of Hazardous Waste, the EPA listed 27 commonly used organic solvents as RCRA hazardous waste when spent or discarded. These spent solvents are identified by EPA Hazardous Waste Numbers F001, F002, F003, F004, and F005. The Administrator had determined that these solvents may pose a substantial present or future hazard to human health or the environment as a result of their ignitability, mobility, persistence, bioaccumulation, and toxicity. (Many of these solvents are carcinogenic, teratogenic, or mutagenic. Others are known to cause chronic health effects.) The solvents were listed as RCRA hazardous waste on the basis of toxicity, ignitability or both.

- o F001 - toxic
- o F002 - toxic
- o F003 - ignitable
- o F004 - toxic
- o F005 - toxic and ignitable

Solvents are considered "spent" when they have been used and are no longer fit for use without further processing. By limiting the scope of the listing to individual spent solvents, in the technical grade or pure form, a major regulatory loophole was created because blends or mixtures containing these solvents were not covered under the listings. At the time, EPA had been unable to establish levels at which a solvent would be considered a "spent solvent" or at which a "spent solvent" would be considered hazardous; therefore, EPA was unable to establish levels at which mixtures of solvents would pose a hazard when spent or discarded. On December 31, 1985, the Agency redefined the universe of hazardous wastes considered spent solvents to include solvent mixtures containing ten percent or more (by volume) of one or more of the listed solvents (50 FR 53315). The Agency believes that the ten percent will bring the majority of solvents used in commerce into the hazardous waste management system since it represents

a level well below concentrations typically used in the solvent formulations. (These mixtures generally contain 50 percent or more of a listed solvent and at least 15 percent chlorinated solvent.) Also, the ten percent threshold is high enough to exclude dilute solvent mixtures. The ten percent or more cutoff for mixtures applies to F001, F002, F004, and F005; ignitable only solvent waste, F003, was excluded. The cutoff was not specified for the F003 mixtures because the Agency could not be assured that at levels below ten percent the waste would not be ignitable. Therefore, spent solvent mixtures containing only F003 solvents are regulated at all concentrations. The amended solvent listings are described as follows:

Industry and EPA Hazardous Waste No.	
F001	The following spent halogenated solvents used in degreasing: tetrachloroethylene, trichloroethylene, methylene chloride, 1,1,1-trichloroethane, carbon tetrachloride, and chlorinated fluorocarbons; all spent solvent mixtures/blends used in degreasing containing, before use, a total of ten percent or more (by volume) of one or more of the above halogenated solvents or those solvents listed in F002, F004, and F005; and still bottoms from the recovery of these spent solvents and spent solvent mixtures.(T)
F002	The following spent halogenated solvents: tetrachloroethylene, methylene chloride, trichloroethylene, 1,1,1-trichloroethane, chlorobenzene, 1,1,2-trichloro-1,2,2-trifluoroethane, ortho-dichlorobenzene, and trichlorofluoromethane; all spent solvent mixtures/blends containing, before use, a total of ten percent or more (by volume) of one or more of the above halogenated solvents or those solvents listed F001, F004, and F005; and still bottoms from the recovery of these spent solvents and spent solvent mixtures.(T)
F003	The following spent non-halogenated solvents: xylene, acetone, ethyl acetate, ethyl benzene, ethyl ether, methyl isobutyl ketone, n-butyl alcohol, cyclohexanone, and methanol; all spent solvent mixtures/blends containing, before use, only the above spent non-halogenated solvents; and all spent solvent mixtures/blends containing, before use, one or more of the above non-halogenated

solvents, and a total of ten percent or more (by volume) of one or more of those solvents listed in F001, F002, F004, and F005; and still bottoms from the recovery of these spent solvents and spent solvent mixtures.(I)*

F004 The following spent non-halogenated solvents: cresols and cresylic acid, and nitrobenzene; all spent solvent mixtures/blends containing, before use, a total of ten percent or more (by volume) of one or more of the above non-halogenated solvents or those solvents listed in F001, F002, and F005; and still bottoms from the recovery of these spent solvents and spent solvent mixtures.(T)

F005 The following spent non-halogenated solvents: toluene, methyl ethyl ketone, carbon disulfide, isobutanol, and pyridine; all spent solvent mixtures/blends containing, before use, a total of ten percent or more (by volume) of one or more of the above non-halogenated solvents or those solvents listed F001, F002, and F004; and still bottoms from the recovery of these spent solvents and spent solvent mixtures.(I)(T)

Summary of the Hazardous and Solid Waste Amendments of 1984 (HSWA) Concerning Solvent Wastes

In its 1984 Hazardous and Solid Waste Amendments (HSWA) to RCRA, Congress directed the EPA to prohibit the continued placement of certain spent solvent wastes (EPA Hazardous Waste Codes: F001, F002, F003, F004, and F005) in or on

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* (I,T) should be used to specify mixtures containing ignitable and toxic constituents.

the land after November 8, 1986.[1] In the event that EPA has not issued regulations by this time, all further land disposal of these spent solvent wastes will be restricted automatically per the HSWA [Section 3004(e)]. Concurrent with the land disposal restrictions, the amendments also require the EPA to promulgate pretreatment regulations for these wastes by November 8, 1986. The amendments specify that wastes treated to the pretreatment level or by the pretreatment method are exempt from the land disposal prohibitions [Section 3004 (m)(1) and (2)].

Summary of the Proposed Solvents Land Disposal Restrictions

On January 14, 1986, the EPA proposed a rule (51 FR 1602) to restrict F001-F005 spent solvents and the corresponding commercial chemical products, manufacturing chemical intermediates or off-specification commercial chemical products [under 40 CFR 261.33 (e) and (f)].[2] Since data indicate that the corresponding commercial solvent products may pose hazards similar to the spent solvents when disposed in Subtitle C facilities, the Agency proposed to exercise its statutory authority and include the corresponding "U" and "P" wastes with restriction decisions on the land disposal of F001-F005 wastes.

To implement the restrictions, the Agency proposed to set treatment standards by deriving individual screening levels for each solvent and a generic liner protection threshold to be applied to all the solvents of concern. The screening levels represent the maximum concentration level below which the Agency believed there would be no harm to human health and the environment if the solvents were land disposed.

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[1]Land disposal for purposes of this regulation includes placement in landfills, land treatment areas, waste piles, and surface impoundments (with certain exceptions for treatment surface impoundments that are double-lined and dredged annually).

[2]Commercial chemical products and manufacturing intermediates are defined as chemical substances which are manufactured or formulated for commercial or manufacturing use. Section 261.33 also lists as hazardous wastes off-specification variants and the residues and debris from the cleanup of spills of these chemicals. Finally, certain containers that have held these chemicals are also hazardous wastes under §261.7. These wastes commonly are referred to as "P" and "U" wastes.

The liner protection threshold is derived from the lowest concentration at which solvents are known to degrade flexible membrane liners. The Agency proposed to restrict F001, F002, F004, and F005 and the corresponding "P" and "U" wastes from land disposal at the screening levels. However, in cases where screening levels for the individual solvents exceeded the liner protection threshold, EPA proposed to specify the liner protection threshold as the treatment standard. Thus, the liner protection threshold would serve as a "safety cap" where screening levels on these solvents were not stringent enough to assure the solvents will not breech liners during the operating life of the facility. EPA proposed the liner protection threshold as the treatment standard for F003 wastes. These solvents were listed as hazardous solely because they exhibit the characteristic of ignitability (toxicity was not a basis for listing). The toxicological data needed to derive screening levels for these solvents have not been evaluated by EPA. Thus, the liner protection threshold was proposed for the F003 wastes since the constituents of these wastes are known to have adverse effects on liners. These adverse effects include swelling or dissolution of synthetic membrane liners and increased permeability of clay soil liners. (Refer to the proposed rule, 51 FR 1602, for more detailed discussions of the proposed land disposal restrictions of solvent waste.)

Summary of Final Solvents Land Disposal Restrictions Rule

The Agency is abandoning the screening level and the liner protection threshold approach proposed on January 14, 1986. Instead, the EPA is promulgating technology-based treatment standards for solvent wastes. These treatment standards are based on the performance that can be achieved using best-demonstrated available technologies. Solvents treated to these levels may be land disposed in Subtitle C facilities. Although the Agency proposed to include the corresponding "U" and "P" wastes, the Agency has not been able to characterize fully these wastes for purposes of the land disposal restrictions. Therefore, decisions on the land disposal of these wastes have been postponed until evaluation of the scheduled wastes (51 FR 19300).

SECTION II

PRODUCTION AND USE OF SOLVENTS

The use of halogenated and nonhalogenated organic chemicals as solvents is widespread throughout the United States and the quantities involved are large. F001 through F005 solvents represent about 95 percent of the organic solvent usage (Ref. 1). Table II-1 summarizes the production of these chemicals in the U.S. during the years 1975, 1980, 1982, and 1984 and the annual growth rate from a base period of 1969-71.

These chemicals are used in a variety of ways in the U.S. economy, such as the following:

- o Chemical feedstocks;
- o Intermediates and carriers in chemical manufacturing (e.g., in dyes and agricultural chemicals);
- o Solvents in surface cleaning and preparation;
- o Solvents in paints, varnishes, and removers of same;
- o Solvents in extraction processes for chemical and food processing;
- o Solvents in textile processing and dry cleaning;
- o Solvents in industrial manufacturing processes; and
- o Aerosol propellants, foam blowing agents, refrigeration brines, flame retardants, etc.

The spent solvent listing covers only those solvents that are used for their "solvent" properties (i.e., their ability to dissolve or mobilize other constituents). Therefore, this document addresses only these uses. Quantitative data on production and use of the solvents of interest are contained primarily in three sources. The most current production and use data are available for six chlorinated solvents (1,1,1-trichloroethane, tetrachloroethylene, methylene chloride, carbon tetrachloride, trichloroethylene and 1,1,2-trichloro-1,2,2-trifluoroethane) from the Integrated Solvents Analysis reported in 1985 by the EPA Office of Toxic Substances (Refs. 2, 3, 4, 5, 6, 7,

TABLE II-1. CHEMICAL PRODUCTION

Solvent	Production, Million lbs/yr 1975	1980	1982	1984	Annual Growth Rate % (Neg)
Acetone	1640	2076	1694	1887	1.7
Butyl alcohol	490	790	730	918	4.8
Carbon disulfide	479	377	261	267	(7.0)
Carbon tetrachloride	908	710	587	600(c)	(3.5)
Chlorobenzene	306	283	237	256	(5.5)
Cresols & cresylic acid	138	143	110	118	(2.5)
Cyclohexanone	554	767	602	796	(0.2)
Di-chlorobenzene(o)	100	124	118	126	(0.5)
Ethyl acetate	171	234	235	210	3.9
Ethyl benzene	4822	7642	6656	8610	3.5
Ethyl ether	(a)				
Isobutanol	158	126	156	164	3.2
Methanol	5176	7153	7555	8280	4.1
Methyl ethyl ketone	425	587	468	556	0.9
Methyl isobutyl ketone	150	168	131	143	(1.2)
Methylene chloride	497	564	532	583(c)	2.9
Nitrobenzene	414	612	775	983	4.1
Pyridine	(b)				
Tetrachloroethylene	679	765	585	550(c)	(1.1)
Toluene	5844	7328	5152	5270	0.4
Trichloroethane(1,1,1)	478	650	556	590(c)	6.0
Trichlorotrifluoroethane (1,1,2-1,2,2)	N/A			130(c)	
Trichloroethylene	293	266	N/A	145(c)	(6.9)
Trichlorofluoromethane	270	158	140	185	(4.2)
Xylene	5155	6650	4818	4964	4.4

(a) 1975 estimate of 28 million lbs down from 100 million lbs in 1970.

(b) 1975 estimate of less than 10 million lbs.

(c) Source: EPA Office of Toxic Substances (Ref. 2)

Source: Reference 9.

8). Current production data for most of the chemical solvents are available from the Predicasts Basebook (Ref. 9), however data on the use of these chemicals as solvents are not provided. The other primary source of use data is an EPA study on most of the solvents of interest issued in 1979 (Ref. 1) which obviously is somewhat dated. The most current data available from any of the three sources are reported in this section. The major solvent-using industries managing these solvents and accounting for about 80 percent of total solvent use reported in this study are as follows (Ref. 1):

Paint & Allied Products and Industrial Operations
Surface Cleaning
Pesticide Production
Laundry and Dry Cleaning Operations
Pharmaceuticals Manufacture

The quantity of individual chemicals used as solvents during 1974 is summarized in Table II-2.

Table II-3 summarizes the use pattern of the 10 most widely used solvents in the industrial categories listed above. These data illustrate the distinct difference between industrial uses of halogenated and non-halogenated solvents. The chlorinated and other halogenated solvents in Table II-3 are used almost exclusively in the surface cleaning, laundry, and dry cleaning categories, whereas the non-halogenated solvents are used primarily in the production categories (paint, pesticides, and pharmaceuticals).

A more detailed discussion of the solvent use in each of the above industry catagories follows:

Paint and Allied Products and Industrial Operations

Solvents are used in the following industrial operations within the Paint and Allied Products and Industrial Operations category:

- o Paint and Allied Products Manufacture
- o Printing Operations
- o Roll Coatings

TABLE II-2. RANKING AND AMOUNTS OF CHEMICALS USED AS SOLVENTS (1974)

Chemical	Amount Used as Solvent (1000's lbs/yr)
Xylenes	1,078,000
Methanol	698,000
Toluene	698,000
Perchloroethylene	563,000
Methylene chloride	469,000
Methyl ethyl ketone	445,000
Trichloroethylene	414,000
1,1,1-Trichloroethane	399,000
Acetone	190,000
Methyl isobutyl ketone	172,000
Chlorobenzene	170,000
Carbon disulfide	170,000
Ethyl acetate	154,000
Ethyl benzene	120,000
Ethyl ether	120,000
n-Butyl alcohol	99,800
1,1,2-Trichloro-1,2,2-trifluoroethane	82,000
Isobutanol	41,000
o-Dichlorobenzene	26,000
Cresols & cresylic acid*	26,000
Cyclohexanone	20,000
Nitrobenzene	20,000
Trichlorofluoromethane	20,000
Pyridine	2,000

* Consumption amounts for cresol and cresylic acid were combined.

Source: Reference 1

TABLE II-3. USE DISTRIBUTION OF THE TEN MOST WIDELY USED ORGANIC SOLVENTS (1974, except footnote b entries 1984)

(All data million lbs per year)

	Xylene	Methanol	Toluene	Perchloroethylene	Methylene chloride	Methyl ethyl ketone	Trichloroethylene	1,1,1-Trichloroethane	Acetone	Methyl isobutyl ketone	Total
Paint and Allied Products	539	660	642	-	25[b]	363	-	16[b]	200	134	2578
Surface Cleaning incl.Electronics	-	-	-	131[b]	96[b]	-	177[b]	460[b]	N/A	-	864
Pesticides	539	-	-	-	25[b]	-	-	10[b]	-	18	591
Pharmaceuticals	N/A	2	55	-	38[b]	N/A	-	N/A	N/A	18	113
Laundry and Dry Cleaning	--	-	-	458	-	-	15	-	-	-	473
TOTAL	1078	662	697	589	184	363	192	486	200	170	
Listed Use Level in Reference (1)	1078	697	697	564	469	444	413	401	189	172	

[a]This total is for the 10 primary solvents only and does not include other solvents used in the respective categories.

[b]Source: EPA Office of Toxic Substances, (Refs. 7, 6, 5, 4, 2).

"N/A" indicates that the solvent at issue probably is used, but the amount is not known.

Source: Reference 1

- o Paper Coatings
- o Dye Manufacture
- o Ink Manufacture
- o Adhesive Manufacture

The Paint and Allied Products and Industrial Operations category historically has accounted for about one-half of all solvent use by industry. The Paint and Allied Products manufacturing portion of this category is the largest solvent-using subcategory. In the 1970's, Printing Operations were the second largest use subcategory.

In the Paint and Allied Products Industry in the 1970's, there were about 1200 paint manufacturing companies that operated more than 1500 plants. Solvents are important ingredients in formulations for solvent-thinned paints, lacquers, and factory-applied coatings. Some solvents are also the primary ingredients in paint and varnish removers.

Spent solvents in the Paint and Allied Products Industry are generated from equipment cleaning. Still bottoms are generated from the recovery of solvents used in the production process. It is estimated that approximately one-third of the solvents used for equipment cleaning are reclaimed, and that 7 million gallons of solvent are disposed annually from this source (Ref. 10). The solvent-containing wastes from the paint industry are primarily non-halogenated solvents such as xylene, methanol, acetone, toluene, and methyl ethyl ketone.

The remaining industrial processes included in this overall category (manufacture of inks, adhesives, dyes, and various types of coatings) utilize primarily non-halogenated solvents in much the same manner as the paint industry; that is, as a component of formulations and for equipment cleaning (Ref. 1). Printing operations use solvents for cleaning operations and as dye or pigment carriers. The types of waste generated from these industries are similar to those from the paint industry and include equipment cleaning wastes and still bottoms from solvent recovery.

Spent solvents from equipment cleaning, if not reclaimed, are drummed and landfilled (Ref. 10). Solvent recovery still bottoms are incinerated, landfilled, or injected into deep wells (Ref. 11).

Surface Cleaning

The major uses of solvents for surface cleaning (including degreasing operations) are in the metal working and service-related industries covered by the SIC (Standard Industrial Classification) codes listed in Table II-4. The total number of solvent degreasing units in use in the United States was estimated to be about 1.1 million units operated by 336,000 plants in 1980 (Ref. 6). Of these, about 221,000 units, or 20% of the total, were estimated to employ chlorinated solvents. It is estimated that about one-half of the solvent degreasers were used by the manufacturing industries such as those involving primary metals, fabricated products, machinery, transportation equipment, and instruments and clocks. The other fifty percent were used by the service-related industries such as auto repair (the largest number of units in service) and railroad and air transportation maintenance. The largest concentrations of these surface cleaning or degreasing operations (54 to 65%) are in the large manufacturing states such as California, Illinois, Massachusetts, Michigan, New Jersey, New York, Ohio, Pennsylvania, and Texas (Ref. 6).

In general, degreasing operations are classified into two basic categories: cold degreasing and vapor degreasing. In cold cleaning operations, the solvent is maintained well below its boiling point. The item to be cleaned is either immersed in the agitated solvent or suspended above the solvent where it is systematically sprayed in a manner similar to that of an automatic dishwasher. Simple cold cleaning operations even may consist of a container of solvent in which items are manually immersed, as is the case in small auto repair shops and in service stations. Cold degreasers use both halogenated and nonhalogenated solvents.

Simple vapor degreasing is achieved by suspending the item to be cleaned above the boiling solvent in a vat. Condensation continues until the temperature of the object approaches that of the solvent vapors. Often the suspended item is sprayed with liquid solvent to facilitate further degreasing. In order to control vapor emissions, a layer of cold air is often maintained above the solvent container. Objects to be cleaned also may be conveyed continuously through the vapor zone. In addition, auxiliary solvent sprays are used to improve the cleaning efficiency of this operation. Vapor degreasers primarily use halogenated solvents as the cleaning media.

TABLE II-4. INDUSTRIES USING HALOGENATED HYDROCARBONS IN DEGREASING OPERATIONS

Source	SIC Code
Metal Furniture	25
Primary Metals	33
Fabricated Products	34
Non-Electric Machinery	35
Electric Equipment	36
Transportation Equipment	37
Instruments and Clocks	38
Miscellaneous Industry	39
Automotive Repair Shops	75
Automotive Dealers	55
Automotive Maintenance Shops	--
Textile Plants (Fabric Scouring)	22
Gasoline Stations	55

Source: Reference 1.

The major solvent used in surface cleaning is 1,1,1-trichloroethane as shown in Tables II-3 and II-5 (Ref. 6). The use of trichloroethylene and methylene chloride has decreased substantially since the late '70's. Most of the solvents used in surface cleaning are halogenated. Their low flammability, high solvency and stability are important characteristics in degreasing and surface cleaning. The consumption of halogenated solvents in surface cleaning/metal degreasing operations in 1984 is indicated in Table II-5.

The annual growth rate in the use of the listed halogenated solvents in degreasing applications is mixed from substantial declines to growth because of differing health and environmental effects. For example, trichloroethylene has been restricted in several states for use in occupational settings because it is a carcinogen (Ref. 12, 13) and it is a contributor to photochemical smogs (Ref. 6). In California, the use of trichloroethylene has been restricted by legislation, but tetrachloroethylene and 1,1,1-trichloroethane are exempt from the restrictions (Ref. 12) and are still used in degreasing operations. Rhode Island has completely banned the use of trichloroethylene (Ref. 13). Also as indicated in Table II-5, the use of carbon tetrachloride has ended because of its high toxicity. According to industry sources the most significant trends in the use of chlorinated solvents for metal cleaning are as follows (Ref. 6):

- Substitution of chlorinated solvents with petroleum-based solvents or alkaline reagents in cold cleaning;
- Substitution of trichloroethylene with 1,1,1-trichloroethane in vapor degreasing;
- Improvement in equipment design and operating procedures to reduce solvent emissions;
- Use of heat pump technology for energy conservation in vapor degreasers.

Although the extent of each of these movements has not been quantitatively determined, the consensus of the sources is that metal degreasing is definitely moving in these directions.

The usefulness of a solvent decreases with time as contaminants adulterate and become concentrated in the solvent. Spent solvent solutions include those solvents that have been used and are no longer fit for use without further processing. These spent solvents are either disposed of as waste, reclaimed and recycled by the waste generator, or processed by a contract solvent reclaiming

TABLE II-5. CONSUMPTION OF HALOGENATED SOLVENTS IN METAL DEGREASING (1984), MILLIONS OF LBS/YR

Solvent	Cold Degreasing	Vapor Degreasing	Total
Carbon tetrachloride	- (a)	- (a)	0
Fluorocarbons	N.A.	N.A.	27
Methylene Chloride	N.A.	N.A.	60
Tetrachloroethylene	30	100	130
Trichloroethylene	17	158	175
Trichloroethane	270	145	415

(a) The blanks indicate that use of carbon tetrachloride has ended because of its high toxicity.

Source: Reference 6

operator. Reclamation is achieved via settling and/or batch distillation. The residue from this process also is covered under the F001-F005 listing.

The composition of spent solvent is dependent on the application of the degreasing operation. Spent solvents may contain up to 90 percent of the original solvent (Ref. 14). Depending on the recovery technique, sludges which result from reclamation processes may contain from 1 to 50 percent of the original hydrocarbon solvent (Ref. 15). However, because of the economic considerations of the reclaiming process, the solvent content of the sludge seldom is reduced below 10 percent. Heavy metal fines and other organics also are present in these wastes, in addition to the original solvent (Ref. 16).

Production of Pesticides, Pharmaceuticals and Other Organic Chemicals

Solvent applications in the production of pesticides, pharmaceuticals, and other organic chemicals include use as a reaction (synthesis) medium and use in equipment cleaning (Ref. 1). The solvents used are primarily non-halogenated and typically are selected for compatibility with the production process. For example, toluene is the most widely used solvent in pharmaceuticals manufacturing; methanol is used as the reaction solvent in Nylon 66 production; and acetone is used as the solvent in the production of cellulose acetate (Ref. 1).

In pesticide formulations, primarily because of cost, overall use of chlorinated solvents have decreased significantly during the past five years. They have been replaced where practicable by aqueous emulsions, deodorized kerosene or other organic solvents, and, to some extent, by dry flowable formulations. Use of methylene chloride currently is significantly greater than that of 1,1,1-trichloroethane. However, recent concern regarding the safety of methylene chloride has led to substitution of 1,1,1-trichloroethane in some products. Use of these two solvents is somewhat interchangeable, although methylene chloride is a significantly better solvent for many pesticide active ingredients. Because of concerns about toxicity, trichloroethylene has been almost completely replaced by other chlorinated hydrocarbons. Use of tetrachloroethylene has decreased sharply for similar reasons. Marketing of carbon tetrachloride-based fumigants has ceased (Ref. 4).

The demand for solvents, especially methylene chloride, by the pharmaceuticals industry, is dependent on the amount of pharmaceutical products produced and probably parallels the fluctuations in pharmaceuticals production. Companies report trying to use less methylene chloride or eliminating its use entirely (Ref. 2). In some chemical production processes, alternatives to use of solvents exist and are in place and in others there appear to be no viable alternatives (Ref. 2).

Methylene chloride is used in several aerosol product categories. It is an important solvent in paints, pesticides, and automotive and industrial aerosol products. Other halogenated solvents also are used in aerosols for paints, pesticides, automotive and industrial products, and laundry spot removers.

Although the number of aerosol cans filled has been fairly constant over the last decade, the use of chlorinated solvents, other than chlorinated fluorocarbons, grew steadily from 1973 to 1982. This growth is due, in part, to the decrease in use of fluorocarbon propellants in aerosols and became more pronounced during 1978-1980 when the use of fluorocarbon propellants in aerosols was banned. Today, hydrocarbon propellants containing chlorinated solvents account for 86% of the markets. However, the use of methylene chloride in aerosols has decreased since 1982, primarily due to its replacement by reformulation and new products in hair sprays (Ref. 3).

In 1983, methylene chloride was used in almost all hair spray formulations, consuming about 30 million pounds, but its use in this application has declined steeply with an estimated consumption in 1984 of 8 to 12 million pounds. It is expected that there will be no methylene chloride (or other chlorinated solvent) in hair sprays in 1986-1988. Methylene chloride is used to a small extent in household products, particularly laundry spot removers (Ref. 3).

Solvents are used as blowing agents in the production of all types of polyurethane foams. Substitutes for the halogenated solvents tend to be solvents with different halogens, i.e. fluorine instead of chlorine. Otherwise there are no other alternatives (Ref. 8).

Solvent wastes generated by these industries are equipment cleaning wastes, solvent recovery still bottoms, and off-specification product materials. (The latter are U or P wastes and are not included in the F001-F005 spent solvent

listing. The U and P solvent wastes will be included in the restrictions at a later date.) A large percentage of these wastes is either reclaimed in-house or by contract recovery operations (Ref. 11) or it is incinerated (Ref. 17).

Solvent-containing wastes from these industries are not as geographically distributed as in the other categories discussed herein, but would be expected to follow the general geographical pattern of the organic chemical industry.

Laundry and Dry Cleaning

The number of dry cleaning plants is declining (Ref. 18). There are about 21,000 retail dry cleaning plants in the United States. About 17,000 of them use perchloroethylene; the others primarily use petroleum solvents such as Stoddard's* solvent, a petroleum distillate. A small amount of fluorinated solvent is used for specialty cleaning (Ref. 18).

The solvents are used to remove dirt, grease and other materials. Dry cleaning solvents are filtered to remove suspended materials and color bodies to allow reuse in the dry cleaning plant. About three quarters of the plants use filter cartridges which are drained and reclaimed or disposed. The rest of the plants use filters requiring a filter aid (diatomaceous earth) and "cookers" or stills for on-site clean-up and recovery of the solvent. The latter process is more complicated, less easily used, and more time consuming to use. The trend is toward the use of filter cartridges (Ref. 18). Still bottoms from retail dry cleaning consist of about 60 percent solvent and 40 percent oily residue (Ref. 19). "Cooker"** residues are 25 percent solvent and 75 percent spent filter aid (mostly diatomaceous earth) (Ref. 19).

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* Stoddard's solvent is not specifically included in the waste listings; however, because this solvent has a flash point of 105°F (i.e., meets the ignitability characteristic), it would also be regulated under the Subtitle C regulatory control system.

** A "cooker" is a type of still in which solvent-contaminated diatomaceous filter aid is heated to drive off the solvent fraction of the total liquid residue contained in the filter aid.

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SECTION III

PHYSICAL/CHEMICAL PROPERTIES OF F001 - F005 CONSTITUENT SOLVENTS

Solvents are used in industry because of their ability to dissolve and mobilize other chemical constituents and to readily volatilize. Yet, when solvents are land disposed, these same factors may cause adverse effects on human health and the environment by degrading liners, mobilizing other hazardous constituents, and volatilizing into the air. These characteristics can be quantified using physical and chemical parameters such as solubility, liquid density, and vapor pressure. In addition, properties relating to biodegradation, bioaccumulation, oxidation, hydrolysis, and photodegradation indicate whether solvents are likely to persist in the environment once they have migrated from the land disposal unit. This section contains a discussion of physical and chemical characteristics of F001 through F005 solvents that are important with respect to the land disposal restrictions regulations and their effects on land disposal.

Vapor Pressure

Vapor pressure is the pressure which is exerted by a gas at equilibrium with its solid and liquid states at a given temperature. The vapor pressure of a solvent may be used as an indication of its volatility. The higher the vapor pressure, the greater the tendency of a solvent to volatilize. Solvents with high vapor pressures may present a substantial risk from air emissions when placed in open disposal areas, i.e., surface impoundments and land treatment (Ref. 11, 18). Coupled with low solubilities, these solvents readily volatilize.

The volatilization rate depends not only on the vapor pressure, but also on the heat of vaporization of the chemical and ambient atmospheric conditions. Heat of vaporization is the energy required to vaporize a solvent and the rate of vaporization will depend on the rate of energy availability. Vapor pressure will limit the extent of vaporization into the atmosphere close to the surface of a land disposal facility, and atmospheric conditions will affect the mixing and removal of solvent vapors that are in the air. The rate and extent of additional solvent vaporization, once there is an equilibrium between the solvent

concentrations in the air and in the land disposal facility, are controlled by the heat of vaporization--the higher the heat of vaporization, the more energy it would take for additional solvent vaporization. For example, methanol and 1,1,1-trichloroethane have approximately the same vapor pressures. However, the heat of vaporization for methanol is over four times that of 1,1,1-trichloroethane. This would mean that when all conditions are in equilibrium in terms of solvent concentrations and atmospheric conditions, it will take more energy to vaporize methanol than to vaporize 1,1,1-trichloroethane. Energy sources for this heat of vaporization include surrounding soils and/or water, incoming materials to the system, and ambient/atmospheric sources particularly the sun.

Once volatilization of a solvent into the air has occurred, atmospheric dispersion may take place. The extent of dispersion of the solvent will depend on both atmospheric conditions and the vapor density of the solvent relative to that of air. (Vapor density is proportional to the molecular weight.) The ability of the solvent to remain in steady-state concentrations in the air, under closed conditions or slow dispersal conditions, is related to the vapor pressure of the solvent and to its original concentration. Table III-1 presents data on the four properties that influence vaporization--molecular weight, vapor pressure, heat of vaporization, and vapor density. For comparative purposes, the data are given for water. Because vapor pressure measurements vary with temperature, an attempt has been made in Table III-1 to report the vapor pressures at temperatures of environmental significance. On the other hand, whatever heat of vaporization data were available have been reported because the heat of vaporization measurements are much less sensitive to temperature variation.

Solvents with high vapor pressures and low solubilities, such as trichlorofluoromethane, carbon disulfide, 1,1,2-trichloro-1,2,2-trifluoroethane, and carbon tetrachloride, are more likely to volatilize into the atmosphere than to remain in the disposal unit (Ref. 11). Once containers or drums holding these solvents corrode, the solvents may volatilize through a landfill cover and pose an air pollution hazard. Solvents with low vapor pressures and high solubilities, such as m-cresol, are likely to remain in the disposal unit. However, because of their high solubilities, these solvents may migrate from the waste matrix to groundwater (Ref. 11).

TABLE III-1. MOLECULAR WEIGHT, VAPOR PRESSURE, AND HEAT OF VAPORIZATION FOR CONSTITUENT SOLVENTS

Constituent Solvent	Molecular Weight*	Vapor Pressure* (mm Hg)	Heat of Vaporization* (cal/g)	Vapor Density (g/L)***
acetone	58.08	200 at 22.7°C or 73°F	131.87 at 20°C or 68°F	2.42
n-butyl alcohol	74.12	4.4 at 20°C or 68°F (12)	--	3.08
carbon disulfide	76.13	260 at 20°C or 68°F (12)	89.35 at 0°C or 32°F 84.09 at 46.25°C or 115°F	3.17
chlorobenzene	112.56	8.8 at 20°C or 68°F (12) 11.8 at 25°C or 77°F (12)	--	4.68
cresols and cresylic acid**	108.13	ortho cresol 0.24 at 25°C or 77°F (12); meta cresol 0.04 at 20°C or 68°F (12); para cresol 0.11 at 25°C or 77°F (12)	meta cresol 100.58 at 202°C or 396°F	4.50
cyclohexanone	98.14	4 at 20°C or 68°F (12)	102.3 (13)	4.08
o-dichlorobenzene	147.01	1.15 at 20°C or 68°F (1) 1.56 at 25°C or 77°F (1)	74.4 (13)	6.12
methylene chloride	84.94	400 at 24.1°C or 75°F (13)	80 at 26°C or 79°F	3.54
ethyl acetate	88.10	72.8 at 20°C or 68°F (12)	102.01 at 0°C or 32°F	3.67
ethyl benzene	106.16	7 at 20°C or 68°F (12)	95.11 at 25°C or 77°F	4.42
ethyl ether	74.12	442 at 20°C or 68°F (12)	83.85 at 34.6°C or 94°F	3.08
isobutanol	74.12	9.0 at 20°C or 68°F (11) 10 at 25°C or 77°F (12)	138.08 at 106.9°C or 224°F	3.08
methanol	32.04	100 at 21.2°C or 70°F	284.29 at 0°C or 32°F 262.79 at 64.7°C or 148°F	1.33

TABLE III-1. MOLECULAR WEIGHT, VAPOR PRESSURE, AND HEAT OF VAPORIZATION FOR CONSTITUENT SOLVENTS (Continued)

Constituent Solvent	Molecular Weight*	Vapor Pressure* (mm Hg)	Heat of Vaporization* (cal/g)	Vapor Density (g/L)***
methyl ethyl ketone	72.10	71.2 at 20°C or 68°F (11) 100 at 25°C or 77°F (9)	105.93 at 78.2°C or 173°F	3.00
methyl isobutyl ketone	100.16 (13)	6 at 20°C or 68°F (12)	116.5 (13)	4.17
nitrobenzene	123.11	0.15 at 20°C or 68°F (11,12) 1 at 44.4° or 112°F (8)	79.08 at 210°C or 410°F	5.12
pyridine	79.10	14 at 20°C or 68°F (12) 20 at 24.8°C or 77°F	107.36 at 114.1°C or 237°F	3.29
tetrachloroethylene	165.85	14 at 20°C or 68°F (12) 19 at 25°C or 77°F (1)	50.05 at 120.7°C or 249°F	7.03
carbon tetrachloride	153.84	89.6 at 20°C or 68°F (11) 113 at 25°C or 77°F (12)	52.06 at 0°C or 32°F 46.42 at 76.75°C or 170°F	6.40 3.83
toluene	92.13	20 at 18.4°C or 65°F 22 at 20°C or 68°F (12)	98.55 at 25°C	
1,1,1-trichloroethane	133.42	100 at 20°C or 68°F (3,11,12,13)	60.1	5.55
trichloroethylene	131.40	60 at 20°C or 68°F (12) 77 at 25°C or 77°F (1)	57.24 at 85.7°C or 186°F	5.47
trichlorofluoromethane	137.37 (13)	687 at 20°C or 68°F (12) 760 at 23.7°C or 75°F (13)	43.10 at 23.82°C or 75°F (13)	5.72
1,1,2-trichloro-1,2,2-trifluoroethane	187.38 (13)	270 at 20°C or 68°F (12)	35.07 at 47.57°C or 118°F (13)	7.80

TABLE III-1. MOLECULAR WEIGHT, VAPOR PRESSURE, AND HEAT OF VAPORIZATION FOR CONSTITUENT SOLVENTS (Continued)

Constituent Solvent	Molecular Weight*	Vapor Pressure* (mm Hg)	Heat of Vaporization* (cal/g)	Vapor Density (g/L)***
xylenes	106.16	ortho xylene 5 at 20.2°C or 68°F, 10 at 32.1°C or 90°F (3,13); meta xylene 5 at 16.8°C or 62°F, 10 at 28.3°C or 83°F (3,13); para xylene 5 at 15.5°C or 60°F, 10 at 27.3°C or 81°F (3,13)	ortho xylene 97.79 at 25°C meta xylene 96.03 at 25°C para xylene 95.40 at 25°C	4.42
water	18.016 (2)	12.8 at 15°C or 59°F 17.5 at 20°C or 68°F 23.8 at 25°C or 77°F 31.4 at 30°C or 86°F	585.6 at 70°F or 21°C (13)	0.75

* Number in parentheses is reference; if no reference number is given then the source was Reference 3.

** Cresylic acid is a mixture of cresols with meta cresol predominating (Ref. 14). Thus the heat of vaporization of meta cresol will probably best represent the heat of vaporization for cresylic acid.

*** Calculated by Pope-Reid Associates, Inc. (St. Paul, MN) using the formula $p_v = \frac{PM}{RT}$ (Ref. 6), where: P = pressure (atm); M = molecular weight; R = ideal gas constant (0.082 atm-L/mol-K); T = temperature (K). This equation assumes that these substances behave like ideal gases. All values are for 20°C or 68°F and a pressure of 1 atm.

The heat of vaporization measurements in Table III-1 show that solvents will evaporate faster than water. The molecular weights show that each of the solvents is more dense than either water vapor or air and thus will disperse into the atmosphere more slowly than water vapor. Finally, the vapor pressures in Table III-1 show that most of the solvents will reach a higher steady-state concentration in air under closed conditions (e.g., in a closed tank or container) or slow dispersal conditions (e.g., under landfill cover materials) than water vapor (3.1 percent at sea level and 77° F). This could cause the listed ignitable solvents F003 and F005 and their constituent solvents to reach their lower flammability limits near ground level under the closed or slow dispersal conditions described above and the listed toxic solvents to reach dangerous concentrations or partial pressures under these conditions.

Solubility and Henry's Law Constant

Solubility is a measure of the mass of a substance that has dissolved in or become miscible with water at a given temperature and pressure. When applied to solvents, this measure may be used as an indication of which solvents are more likely to enter into the aqueous phase and how fast they would enter that phase. The solubility of a solvent in water depends primarily on ambient temperature.

Many organic solvents are considered to be insoluble in water. However, each of the listed solvents is soluble in water to some extent and some are completely miscible. In general, many of the halogenated solvents are less soluble than the non-halogenated solvents. Solvents such as chlorobenzene, carbon tetrachloride, tetrachloroethylene, and o-dichlorobenzene have low solubilities, while non-halogenated solvents such as pyridine, methyl ethyl ketone, and isobutanol have very high solubilities (see Table III-2) (Ref. 11).

Several of the solvents have relatively low solubilities in water and relatively high vapor pressures. In these cases the water solubility of the constituent solvent depends on both the temperature and the vapor pressure rather than on the temperature alone. For these solvents another parameter, the Henry's law constant, can be very important. The Henry's law constant is the partial pressure of the solvent in the vapor phase--approximately the concentration in the adjacent atmosphere--divided by its concentration in the liquid phase. When this constant is low at any temperature, the solvent has a high solubility and

TABLE III-2. SOLUBILITIES IN WATER AND HENRY'S LAW CONSTANTS FOR CONSTITUENT SOLVENTS

Constituent Solvent	Solubility in Water* (mg/l)	Henry's Law Constant* ($atm\text{-}m^3/mole$)
acetone	miscible in all proportions	5.86×10^{-5} (17)**
n-butyl alcohol	77,000 (12)	8.90×10^{-6} (28)
carbon disulfide	2300 at 22°C or 72°F (12)	1.68×10^{-2} ***
chlorobenzene	500 at 20°C or 68°F (12)	3.46×10^{-3} (4)
cresols and cresylic acid	ortho cresol 31,000 at 40°C or 104°F (12); meta cresol 23,500 at 20°C or 68°F (12); para cresol 24,000 at 40°C or 104°F (12); cresylic acid between 24,000 and 31,000 at 40°C or 104°F (11)	m = 5.05×10^{-6} *** acid = 5.05×10^{-6} ***
cyclohexanone	23,000 at 20°C or 68°F (12)	3.50×10^{-5} **
o-dichlorobenzene	140 at 20°C or 68°F (12) 145 at 25°C or 77°F (12)	1.88×10^{-3} (4)
methylene chloride	20,000 at 20°C or 68°F (2,3,12) 16,700 at 25°C of 77°F (12)	3.19×10^{-3} (16)
ethyl acetate	80,800 between 20 and 25°C or 68 and 77°F (11)	1.23×10^{-4} ***
ethyl benzene	152 at 20°C or 68°F (12)	6.44×10^{-3} (7,28)
ethyl ether	69,000 at 20°C or 68°F (12) 60,500 at 25°C or 77°F(12)	8.90×10^{-4} ***
isobutanol	95,000 at 18°C or 64°F (12)	1.23×10^{-5} ***
methanol	miscible in all proportions	6.47×10^{-6} (17)**
methyl ethyl ketone	353,000 at 10°C or 50°F (12) 292,000 between 20 and 25°C or 68 and 77°F (11)	2.61×10^{-5} ***
methyl isobutyl ketone	17,000 at 20°C or 68°F (12) 19,000 at 25°C or 77°F (12)	4.63×10^{-5} (28)**
nitrobenzene	1900 at 20°C or 68°F (12)	2.40×10^{-5} (16)
pyridine	miscible in all proportions	1.95×10^{-7} ****
tetrachloroethylene	150 at 20°C or 68°F (1)	2.87×10^{-2} (16)

TABLE III-2. SOLUBILITIES IN WATER AND HENRY'S LAW CONSTANTS FOR CONSTITUENT SOLVENTS (Continued)

Constituent Solvent	Solubility in Water* (mg/l)	Henry's Law Constant* (atm-m^3/mole)
carbon tetrachloride	800 at 20°C or 68°F (12) 1160 at 25°C or 77°F (12)	1.97×10^{-2} (4)
toluene	470 at 16°C or 61°F (12) 515 at 20°C or 68°F (12)	5.93×10^{-3} (16)
1,1,1-trichlorethane	4400 at 25°C or 77°F (12)	2.76×10^{-2} (4)
trichlorethylene	1000 at 20°C or 68°F (1) 1100 at 25°C or 77°F (12)	1.17×10^{-2} (16)
trichlorofluoromethane	1100 at 25°C or 77°F (12,13)	8.02×10^{-1} (4)
1,1,2-trichloro-1,2,2-trifluoroethane	1700 at 25°C or 77°F (13)	9.00 *****
xylenes	ortho xylene 175 at 20°C or 68°F (12) para xylene 198 at 25°C or 77°F (12)	o = 4.94×10^{-3} (4) p = 7.00×10^{-3} (4) m = 6.91×10^{-3} (4)

* Numbers in parentheses indicate references.

** Calculated using activity coefficient (AC) estimated by the UNIFAC method (Ref. 26) using the equation $H_c = (0.000018)(AC)(P_{vap})$.

*** Calculated from solubility and vapor pressure data using the procedure outlined in Reference 4. For solvents that are gases at 25°C a value of 1.0 atm was used for the vapor pressure.

**** Calculated from solubility (Ref. 29) and vapor pressure (Ref. 30) data.

***** Calculated from solubility and vapor pressure data using solubility estimated from hexachloroethane (Ref. 27)

little tendency to evaporate. On the other hand, a high Henry's law constant means that at any temperature the solvent has a low solubility and exhibits a high tendency to evaporate at a given pressure. The solubilities in water and the Henry's law constant in water for the constituent solvents are presented in Table III-2.

As shown in Table III-2, the water solubilities and Henry's law constants vary quite markedly for the different individual solvents. Although a few solvents are soluble in water only to the extent of a few hundred parts per million (e.g., ethyl benzene, toluene, and xylene), several solvents are soluble in water to the extent of 1.6 to over 35 percent or are completely miscible with water (e.g., methanol and pyridine).

Solvents that possess high solubility values will enter into the aqueous phase more readily than solvents with low solubility values. Hence, solubility may be used to indicate the potential of a solvent to migrate into and remain in the groundwater beneath a land disposal facility (Ref. 11). Examples of such solvents are methyl ethyl ketone, isobutanol, n-butyl alcohol, and ethyl acetate. Solvents such as tetrachloroethylene, carbon tetrachloride, and trichlorofluoromethane have high Henry's law constants in water. This indicates that they could vaporize quite easily from aqueous environments. Thus, these solvents would be expected to vaporize from treatment or storage surface impoundments into the atmosphere, possibly causing air pollution problems.

Liquid Density

Liquid density is a measure of the mass per unit volume of a liquid solvent. Liquid density may be used as an indication of the amount of solvent which does not solubilize into an aqueous solution but forms as a concentrated layer either above or below the aqueous phase (Ref. 11). .As a practical matter, this means that excess solvent could phase separate from the waste matrix and collect into a separate concentrated liquid layer (Ref. 8). A solvent that is less dense than water may float to the surface of a hazardous waste surface impoundment, increasing the possibility that it may vaporize, ignite, or come into direct contact with humans or other lifeforms. A solvent that is more dense than water may sink to the bottom of a surface impoundment, increasing the possibility that it may come into direct contact with the liner system and possibly damage it.

Table III-3 presents the liquid densities of the F001 through F005 solvents. For comparative purposes the density of air-free water is 0.998 g/cc at 20°C or 68°F and 1.00 g/cc at 4°C or 39°F (Ref. 2, 3, 13). In general, the ignitable solvents will tend to float on water while the chlorinated solvents will tend to sink. Halogenated solvents generally are less soluble and more dense than non-halogenated solvents (Ref. 15).

Dielectric Constant

The dielectric constant is a measure of the ability of a solvent to reduce the attraction between positive and negative solute ions. Substances (such as clay liners) that are swollen to a gel state by a liquid of one dielectric constant (e.g., water), will flocculate when they come into contact with a liquid of a much lower dielectric constant (e.g., organic solvent). Table III-4 shows the dielectric constants of the solvents. For comparative purposes the dielectric constant of water is between 78.3 (Ref. 2) and 78.54 (Ref. 13) at 25°C or 77°F. Because many of the clays used for landfill liners absorb water and swell, liquids with dielectric constants lower than about 50 will attack clay liners of land disposal units. All of the solvents listed in Table III-4 have dielectric constants much lower than 50 and may attack many clay liner systems. The degree and rate of attack will be influenced by the solvent concentration in the waste.

Octanol/Water Partition Coefficient

The log of the octanol/water partition coefficient is a measure of the tendency of an organic material (e.g., a solvent) to escape from water. Hydrophilic (soluble) solvents would have lower log octanol/water partition coefficients than would hydrophobic (insoluble) solvents (Ref. 25). This would mean that the hydrophobic solvents (with log octanol/water partition coefficients of two to four) would be more likely to adsorb onto clay soils in the presence of water than to pass through the soils. Examples of these solvents are xylene, trichloroethylene, and chlorobenzene, as shown in Table III-5. Solvents such as acetone, cyclohexanone, and methanol, with log octanol/water partition coefficients of less than one, would be expected to move with water through clay soils. Thus, it would be expected that solvents with low log octanol/water partition

TABLE III-3. LIQUID DENSITIES OF CONSTITUENT SOLVENTS

Constituent Solvent	Density of the Liquid* (g/ml)
acetone	0.791 (2)
n-butyl alcohol	0.810
carbon disulfide	1.26 (3)
chlorobenzene	1.11 (2)
cresols and cresylic acid	ortho cresol-1.05 (3) meta cresol-1.03 (3) para cresol-1.04 (3) cresylic acid-1.03 to 1.04 (11)
cyclohexanone	0.947 at 19°C or 66°F
o-dichlorobenzene	1.31 (2)
methylene chloride	1.34
ethyl acetate	0.901
ethyl benzene	0.867
ethyl ether	0.708 at 25°C or 77°F
isobutanol	0.802 (2)
methanol	0.792
methyl ethyl ketone	0.805 0.798 (13)
methyl isobutyl ketone	0.802(12)
nitrobenzene	1.20 (2)
pyridine	0.98 (2)
tetrachloroethylene	1.63 at 15°C or 59°F (2)
carbon tetrachloride	1.59 (2)
toluene	0.87
1,1,1-trichloroethane	1.35 at 15°C or 59°F (2) 1.33 at 26°C or 79°F (3)
trichloroethylene	1.46

TABLE III-3. LIQUID DENSITIES OF CONSTITUENT SOLVENTS (Continued)

Constituent Solvent	Density of the Liquid* (g/ml)
trichlorofluoromethane	1.47 at 25°C or 77°F (13)
1,1,2-trichloro-1,2,2-trifluoroethane	1.57 at 25°C or 77°F (13)
xylenes**	ortho xylene 0.880 (2) meta xylene 0.864 (2) para xylene 0.861

* All densities are at 20°C or 68°F unless otherwise indicated; references indicated by numbers in parentheses; if no reference number is given then the source was both References 2 and 3.

** The commercial xylenes product is predominantly meta xylene (Ref. 14) and could be expected to have an intermediate density.

TABLE III-4. DIELECTRIC CONSTANTS OF CONSTITUENT SOLVENTS*

Constituent Solvent	Dielectric Constant**
acetone	20.70 at 25°C or 77°F
n-butyl alcohol	17.8 at 20°C or 68°F (13) 17.1 at 25°C or 77°F
carbon disulfide	2.641 at 20°C or 68°F
chlorobenzene	5.708 at 20°C or 68°F (13) 5.621 at 25°C or 77°F (13)
cresols and cresylic acid	ortho cresol 11.5 at 25°C or 77°F meta cresol 11.8 at 25°C or 77°F para cresol 9.91 at 58°C or 136°F
cyclohexanone	18.3 at 20°C or 68°F
o-dichlorobenzene	9.93 at 25°C or 77°F
methylene chloride	9.08 at 20°C or 68°F
ethyl acetate	6.02 at 25°C or 77°F
ethyl benzene	2.412 at 20°C or 68°F (13)
ethyl ether	4.335 at 20°C or 68°F
isobutanol	17.7 at 25°C or 68°F (13)
methanol	32.63 at 25°C or 77°F (13) 32.70 at 25°C or 77°F (2)
methyl ethyl ketone	18.51 at 20°C or 68°F (13)
methyl isobutyl ketone	13.11 at 20°C or 68°F (2)
nitrobenzene	35.74 at 20°C or 68°F 34.82 at 25°C or 77°F
pyridine	12.3 at 25°C or 77°F
tetrachloroethylene	2.30 at 25°C or 77°F (2)
carbon tetrachloride	2.238 at 20°C or 68°F

TABLE III-4. DIELECTRIC CONSTANTS OF CONSTITUENT SOLVENTS (Continued)*

Constituent Solvent	Dielectric Constant**
toluene	2.38 at 20°C or 68°F (2) 2.379 at 25°C or 77°F (13)
1,1,1-trichloroethane	7.6 at 20°C or 68°F (2)
trichloroethylene	3.42 at 16° or 61°F
trichlorofluoromethane	2.28 at 29°C or 84°F (13)
1,1,2-trichloro-1,2,2-trifluoroethane	2.41 at 25°C or 77°F (13)
xylenes	ortho xylene 2.568 at 20°C or 68°F (13) meta xylene 2.374 at 20°C or 68°F (13) para xylene 2.270 at 20°C or 68°F (13)

* The dielectric constant listed in this table is the static value or low frequency value for the constituent solvent in the liquid state at atmospheric pressure; pressure, however, has very little effect on the dielectric constant of a liquid.

** References indicated by number in parentheses; if no reference number is given then the source was both References 2 and 13.

TABLE III-5. LOG OCTANOL/WATER PARTITION COEFFICIENTS OF CONSTITUENT SOLVENTS

Constituent Solvent	Log Octanol/Water Partition Coefficient*
acetone	-0.24 (31)
n-butyl alcohol	0.88 (12)
carbon disulfide	2.16 (31)
chlorobenzene	2.87 (31)
cresols and cresylic acid	ortho cresol 2.04 (24) meta cresol 2.01 (12,24) para cresol 1.94 (12), 1.99 (24) cresylic acid 2.04 (24)
cyclohexanone	0.86 (31)
ortho dichlorobenzene	3.58 (31)
methylene chloride	1.26 (31)
ethyl acetate	0.71 (31)
ethyl benzene	3.36 (31)
ethyl ether	1.32 (31)
isobutanol	0.75 (12), 0.90 (9)
methanol	-0.75 (31)
methyl ethyl ketone	0.30 (31)
methyl isobutyl ketone	1.25 (31)
nitrobenzene	1.90 (31)
pyridine	0.70 (31)
tetrachloroethylene	3.03 (31)
carbon tetrachloride	2.96 (31)
toluene	2.82 (31)
1,1,1-trichloroethane	2.20 (9)
trichloroethylene	2.28 (31)
trichlorofluoromethane	2.52 (31)
1,1,2-trichloro-1,2,2-trifluoroethane	3.10 (31)
xylenes	meta xylene 3.20 (12) para xylene 3.15 (12)

* References indicated by numbers in parentheses.

coefficients would move readily through clay liner systems at land disposal facilities. The chlorinated solvents and the aromatic solvents generally have higher log octanol/water partition coefficients and would tend to bioaccumulate.

Persistence and Bioaccumulation

Many organic chemicals can be degraded by biological processes, oxidation or reduction, hydrolysis, or photolysis. Furthermore, certain soils may attenuate the concentration of solutes, normally by adsorption, but sometimes by absorption. In parts of the natural environment the degradation processes may not occur at all or may occur slowly. For example, deep groundwater is abiotic and often close to neutral pH so that biodegradation, photolysis, and hydrolosis do not occur. Even under suitable degradation conditions some of these constituent solvents are very persistent. The following two subsections briefly describe biodegradation/bioaccumulation and oxidation/hydrolysis/photodegradation. A subsection containing specifics of these parameters as they relate to the constituent solvents follows:

Biodegradation/Bioaccumulation

Biodegradation is the degradation of a substance caused by biochemical reactions from microorganisms in soil and water. Non-halogenated solvents appear to be more readily biodegradable than halogenated solvents. Two examples of biodegradable non-halogenated solvents are cresols/cresylic acid and methyl ethyl ketone. Conversely, many of the halogenated solvents, such as o-dichlorobenzene, 1,1,1-trichloroethane, and methylene chloride, are less biodegradable or non-biodegradable. The halogenation of a compound may render it less biodegradable or nonbiodegradable (Ref. 11). There are two reasons for this. The first is that halogenated solvents are generally very toxic, and they may eliminate the biodegrading organisms before the organisms can metabolize the solvent. The second is that the enzymes produced by biodegrading organisms can more readily break down the types of molecular bonds found in non-halogenated solvents than the carbon-halogen bonds found in halogenated solvents. As a class of chemicals, solvents do not appear to biodegrade very readily. This has several implications for land disposal; if a solvent migrates from a land disposal facility it is likely to persist in the environment for long periods of time.

Persistence of a solvent in the environment may lead to bioaccumulation if the solvent is ingested. Bioaccumulation is the process in which concentrations of a substance are progressively increased as the substance moves through the successive links of the food chain. Solvents that have low water solubilities are more likely to bioaccumulate than solvents with high water solubilities. Data on bioaccumulation are limited.

Oxidation, Hydrolysis, and Photodegradation

A compound may be broken down into simpler compounds through oxidation, hydrolysis, and/or photodegradation. Oxidation is a process in which a compound absorbs and reacts chemically with an oxidant such as oxygen (O_2). Hydrolysis occurs as a result of an introduction of a hydroxyl function (OH-) into the compound and a deletion of a halogen, nitrate, or amine from the compound. Photodegradation occurs when sunlight is absorbed by the compound and causes the compound to undergo reaction. The majority of the solvents, however, do not appear to be significantly affected by these processes.

Examples of Persistence and Bioaccumulation of F001 - F005 Solvents

Carbon disulfide is not known to attenuate in soils. Therefore, it could leach into the groundwater, where, being unamenable to hydrolysis, it is likely to persist for an extended time period (Ref. 9).

Chlorobenzene is not amenable to hydrolysis and does not biodegrade well, and therefore it is very persistent in the environment (Ref. 9). It also has a great tendency to bioaccumulate (Ref. 22).

Cresols, once dissolved in water, can rapidly form chlorinated compounds, which are more environmentally objectionable. Cresols are not known to hydrolyze and thus are likely to persist in groundwater (Ref. 9).

Ortho-dichlorobenzene was demonstrated to be persistent in air, water, and soil at Love Canal (Ref. 23). Ortho-dichlorobenzene has a high bioaccumulation potential, and thus, migration of small concentrations could pose a hazard (Ref. 19).

Methylene chloride could present an air pollution problem because of its high

volatilization rate (1.8 times the rate of ether) and its stability (and therefore possibly persistence) in air and light. In addition, it is stable in water and possibly persistent in groundwater (Ref. 9).

Isobutanol does not readily persist in the environment. However, if it contaminates surface water, isobutanol may adversely affect the water's self-purification ability (Ref. 9) by adding to contaminant loading and inhibiting biodegradation.

Methyl ethyl ketone, because of its high vapor pressure and high water solubility, may cause both air and water pollution problems. It was demonstrated to be persistent in air and groundwater at Love Canal (Ref. 23).

Nitrobenzene is likely to be highly persistent in groundwater because it is not amenable to hydrolysis and does not biodegrade well (Ref. 9).

Pyridine should not be attenuated unless the soil has sufficient cation exchange capacity from high clay content (Ref. 9). Pyridine also would be likely to persist in the abiotic environment of most groundwaters.

Tetrachloroethylene was demonstrated to be very mobile and persistent in air, water, and soil at Love Canal (Ref. 23).

Carbon tetrachloride should be very persistent and thus is not likely to be biodegradable.

Toluene should be persistent in abiotic environments such as most aquifers. It was demonstrated to be persistent in air, water, and soil at Love Canal (Ref. 23).

1,1,1-trichloroethane poses both air and water pollution problems. Once in the air, it will decompose only at elevated temperatures. 1,1,1-trichloroethane is reactive in sunlight at high altitudes, but stable at low altitudes. It is not easily attenuated, particularly where soils are low in inorganic content. It is also relatively persistent in groundwater where it reacts or hydrolyzes slowly, releasing hydrochloric acid (Ref. 9).

Trichloroethylene was demonstrated to be persistent in air at Love Canal (Ref. 23).

Trichlorofluoromethane and 1,1,2-trichloro-1,2,2-trifluoroethane are very persistent in the environment due to resistance to biodegradation, photodecomposition, and chemical degradation. Because of their persistence, after release at the surface of the earth, these two solvents eventually rise to the stratosphere where they may release chlorine atoms and deplete the ozone layer. This can lead to various adverse health and environmental effects resulting from an increase in the amount of ultraviolet radiation reaching the earth, as well as possible changes in the earth's climate induced by the "greenhouse effect" (Ref. 20,21).

Ignitability

The F003 and F005 solvents were listed as hazardous wastes because of the property of ignitability, and ignitability and toxicity, respectively. The RCRA hazardous waste regulations define ignitable liquids as those liquids containing less than 24 percent alcohol by volume and having a flash point of less than 140°F as determined in a Pensky-Martin Closed Cup test. The flash points of the F003 and F005 solvents listed on the basis of ignitability are shown in Table III-6. It should be noted that ignitable wastes currently may not be land disposed unless they are rendered non-ignitable or are containerized (CFR 265.312).

Other parameters that provide useful information about an ignitable waste are the flammability limits, the heating value, and the percentage of chlorine in the waste. The flammability limits are the range of concentrations suitable to propagate a flame if the ambient temperature is above the flash point and there is a source of ignition present. A waste that has wide flammability limits has a large range of concentrations in air which will support combustion, such as n-butyl alcohol (flammability limits of 1.45 to 11.25 volume percent in air). If the waste has a high net heating value there is a danger of explosion, spreading of a fire that has started, or vaporizing toxic constituents in other co-disposed wastes. Burning wastes that have a high chlorine content may emit large amounts of toxic chlorine, thereby increasing the hazard. The flammability limits, heating value, and percent chlorine are presented in Table III-7. The chlorinated solvents have relatively lower heating values than the nonchlorinated solvents and should be less likely to explode in a fire. A fire can cause the vaporization of toxic solvents and thus lead to environmental dispersion through the atmosphere.

TABLE III-6. FLASH POINTS OF IGNITABLE CONSTITUENT SOLVENTS*

Constituent Solvent	Flash Point**
acetone	-18°C or 0°F (14)
n-butyl alcohol	36 to 38°C or 97 to 100°F (14)
carbon disulfide	-30°C or -22°F (14)
chlorobenzene	28°C or 82°F (14)
cyclohexanone	111°F (10), 147°F (14)
ethyl acetate	7.2°C or 45°F (14)
ethyl benzene	18°C or 64°F (14)
ethyl ether	-45°C or -40°F (14)
isobutanol	28°C or 82°F (14)
methanol	12°C or 54°F (14)
methyl ethyl ketone	22°F (10), 35°F (14)
methyl isobutyl ketone	61°F (5)
pyridine	74°F (14), 23°C(11)
toluene	4.4°C or 40°F (14)
xylenes	ortho xylene 17°C or 63°F (14) meta xylene 25°C or 77°F (14) para xylene 25°C or 77°F (14) xylene 29°F or 84°F (14) mixed meta and para 100°F (10)

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* A solvent is listed in this table if its flash point is less than or equal to 60°C or 140°F.

** Reference indicated by number in parentheses.

TABLE III-7. HIGHER HEATING VALUES, PERCENT CHLORINE, AND FLAMMABILITY LIMITS OF CONSTITUENT SOLVENTS

Constituent Solvent	Higher Heating Value* (kcal/g)	Percent Chlorine**	Flammability Limits (volume percent in air)***
acetone	7.368 at 25°C or 77°F	0	2.25 to 12.80 (13); 2.5 to 13.0 (2)
n-butyl alcohol	8.628 at 25°C or 77°F	0	1.45 to 11.25 (13)
carbon disulfide	3.239 at 20°C or 68°F	0	1 to 50 (14); 1.25 to 50.00 (13); 1.2 to 73.0 (2)
chlorobenzene	--	31.50	1.3 to 7.1 (10)
cresols and cresylic acid	ortho cresol 8.162; meta cresol 8.143; para cresol 8.161	0	--
cyclohexanone	--	0	Lower 1.1 @ 100°F (10)
o-dichlorobenzene	4.570	48.24	--
methylene chloride	1.257 vapor	83.49	--
ethyl acetate	6.094	0	2.18 to 11.40 (13); 2.2 to 11.5 (14)
ethyl benzene	10.28	0	1.0 to 6.7 (10)
ethyl ether	--	0	1.85 to 36.50 (13); 1.8 to 36.5 (2)
isobutanol	8.610	0	Lower 1.68 (13)
methanol	5.419 at 25°C or 77°F	0	6.0 to 36.5 (14); 6.72 to 36.50 (13); 6.7 to 50 (2)
methyl ethyl ketone	8.102 at 25°C or 77°F	0	1.81 to 9.50 (13); 1.8 to 10 (10)
methyl isobutyl ketone	--	0	--
nitrobenzene	6.004	0	--
pyridine	8.407	0	1.81 to 12.40 (13); 1.8 to 12.4 (10)
tetrachloroethylene	--	85.52	--
carbon tetrachloride	0.2425	92.19	--
toluene	10.14	0	1.27 to 6.75 (13); 1.0 to 7.3 (2); 1.27 to 7 (10)

TABLE III-7. HIGHER HEATING VALUES, PERCENT CHLORINE, AND FLAMMABILITY LIMITS OF CONSTITUENT SOLVENTS (Continued)

Constituent Solvent	Higher Heating Value* (kcal/g)	Percent Chlorine**	Flammability Limits (volume percent in air)***
1,1,1-trichloroethane	--	79.72	--
trichloroethylene	--	80.95	--
trichlorofluoromethane	--	77.43 (also 13.83% fluorine and 91.25% all halogens)	--
1,1,2-trichloro-1,2,2-trifluoroethane	--	--	
xylenes****	ortho xylene 10.28 meta xylene 10.25 para xylene 10.26	0	ortho xylene 1.0 to 6.0 (13,10) meta xylene 1.1 to 7.0 (10) para xylene 1.1 to 7.0 (10)

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* All higher heating values are for liquid solvents at 20°C or 68°F, except as noted; all higher heating values are from Reference 13.

** All percent chlorine data are from Reference 14.

*** Numbers in parentheses are references; values from Reference 2 are at 25°C or 77°F and 760 mm Hg; values from Reference 13 are at room temperature and atmospheric pressure.

**** The commercial xylene is a mixture in which meta xylene predominates (Ref. 14). Thus the commercial xylene mixture should have a higher heating value similar to that of meta xylene.

Mobilization of Other Hazardous Constituents

Solvents are used in commerce primarily for their solvent properties; that is, their ability to dissolve (solubilize) or disperse (mobilize) other substances. For example, a study conducted on PCB-contaminated soils demonstrated that more than 95 percent of the PCBs were extracted from these soils using acetone as a solvent (Ref. 32).

A recent study conducted by the Agency supports the claim that solvents may increase the mobility of other compounds (Ref. 33). The study demonstrated that wastes containing aromatic solvents and chlorinated solvents, as well as surfactants (none as free liquids), generally increase the mobility of compounds adsorbed onto a synthetic waste. Decrease in mobility of some compounds was also observed. Wastes such as electroplating waste, API separator sludge, lime-stabilized waste and an unstabilized sludge were used in the study. However, due to the complexity and diversity of these wastes some chromatographic interferences and reproducibility problems occurred. (The wastes contained high concentrations of a variety of solvents.) Table III-8 provides a summary of data on the mobilization results obtained with three of the wastes in the study. Therefore the Agency is contemplating doing further research and applying synthetic waste using a standard leaching solution with single solvents or binary mixtures of common organic solvents added at low levels. Such a protocol will assure homogeneity and allow for stability testing. Information from the study could then be used to assess and possibly predict the solvent power of common organic solvents at low levels. In addition, it will enable the Agency to better determine the ability of commonly used organic solvents (i.e., those likely to be found in land disposal sites) to increase the mobility of other hazardous compounds. Moreover, the Agency will be able to ascertain whether low solvent concentrations will likewise mobilize other hazardous constituents.

TABLE III-8. COMPARISON OF RECOVERY OF TARGET COMPOUNDS IN WASTE MOBILIZATION STUDY

Target Compound	Electroplating Waste		Unstabilized Sludge		API Separator Sludge	
	% Recovery by the Waste	% Recovery by Control	% Recovery by the Waste	% Recovery by Control	% Recovery by the Waste	% Recovery by Control
N-Nitroso-di-N-propylamine	70	92	100	92	125	92
2-Nitrophenol	66	81	9	81	53	81
Naphthalene	34	52		52	111	52
Quinoline	57	68	42	68	79	68
n-Chloro-p-cresol	43	71		71	55	71
2,4,6-Trichloro-phenol	42	51	70	51	31	51
Acenaphthene	19	40	17	40	0	40
N-Nitrosodi-phenylamine	50	38	45	38	0	38
Lindane	0	34	40	34	14	34
Anthracene	0	0	13	0	2	0
Heptachlor	0	7	12	8	0	8
Aldrin	0	8	11	9	7	9
Pyrene	0	0	9	0	0	0
Endrin	2	6	12	6	8	6
Bis(2-ethylhexyl) phthalate	0	10	3	10	3	10
Benzo(k)fluoran-thene		0		0	0	0

Source: Reference 33

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SECTION IV

TOXICITY OF LISTED SOLVENTS

Many of the listed solvents are carcinogenic, teratogenic, mutagenic, or neurotoxic. Others are known to cause other chronic health effects. The toxicity of each of the F001 through F005 solvents is summarized in this section.

Carbon Disulfide

Short-term human exposure to low atmospheric concentrations of carbon disulfide may result in central nervous system depression, headaches, breathing difficulty, and gastrointestinal disturbances. Exposure to short-term but high atmospheric concentrations can lead to narcosis and death. The symptoms of humans subjected to repeated exposure to high concentrations or prolonged exposure to low concentrations of carbon disulfide include insomnia, fatigue, loss of memory, headache, melancholia, vertigo, and loss of appetite. Visual impairment, loss of reflexes, and lung irritation have been reported (Ref. 38,39). Rats and mice exposed eight hours per day for 20 weeks to an average concentration of 37 ppm carbon disulfide showed evidence of toxic effects (Ref. 1,38).

Chlorobenzene

Chlorobenzene has been found to produce histopathological changes in the lungs, liver, and kidneys following its inhalation by rats, rabbits, and guinea pigs (Ref. 9). Oral administration of chlorobenzene to rats was reported to cause growth retardation in males (Ref. 12). Chlorobenzene also appears to increase the activity of some microsomal enzyme systems, which enhances the metabolism of many drugs, pesticides, and other xenobiotics (Ref. 1,28). Chlorobenzene was reported to be toxic to varying degrees to several fresh- and salt-water organisms, including algae (Ref. 32).

Cresols and Cresylic Acid

Cresols are highly toxic if orally administered and moderately toxic if inhaled. Absorption may result in damage to kidneys and liver as well as to the central

nervous system (Ref. 39). Exposure to cresols can cause severe skin burns and dermatitis (Ref. 1,38,39).

Ortho-Dichlorobenzene

Ortho-dichlorobenzene exhibits moderate toxicity via inhalation and oral routes. The major toxicological effect is injury to the liver and kidneys. It is also a central nervous system depressant after short periods of exposure (Ref. 1,38,39).

Methylene Chloride

A study by the National Institutes of Health has shown that methylene chloride should be considered a probable human carcinogen, Group B2 (Ref. 41). It is a carcinogen in two species of laboratory animals--rats and mice. Inhalation of methylene chloride has caused liver and lung adenomas and carcinomas in both sexes of mice (Ref. 41). Methylene chloride also was reported as being mutagenic to a bacterial strain, S. typhimurium (Ref. 25). It was reported to be feto- or embryo-toxic to rats and mice (Ref. 24). Female workers had gynecological problems after prolonged exposure to methylene chloride (Ref. 37). Methylene chloride also causes central nervous system depression and elevation of carboxyhemoglobin levels (Ref. 20). Severe methylene chloride contamination of food or water can cause irreversible renal and hepatic injury (Ref. 31). Acute toxicity values range from 147,000 to 310,000 ug/l for aquatic organisms (Ref. 1).

Isobutanol

Rats receiving isobutanol, either orally or subcutaneously, one to two times per week for 495 to 643 days showed liver carcinomas and sarcomas, spleen sarcomas, and myeloid leukemia (Ref. 7). Ingestion of a one-molar solution of isobutanol in water by rats for four months did not produce any inflammatory reaction of the liver. However, rats ingesting a two-molar solution for two months developed Mallory's alcoholic hyaline bodies in the liver and were observed to have decreases in fat, glycogen, and RNA in the liver (Ref. 7). Acute exposure to isobutanol causes narcotic effects and irritation to the eyes and throat in

humans exposed to 100 ppm for repeated eight-hour periods. Formation of vacuoles in the superficial layers of the cornea and loss of appetite and weight were reported among workers subjected to an undetermined, but apparently high, concentration of isobutanol (Ref. 26).

Methyl Ethyl Ketone

Methyl ethyl ketone is of moderate toxicity via ingestion. It can affect the peripheral nervous system and is an experimental teratogen (Ref. 1). It is also a strong irritant of the mucous membranes of the eyes and nose. A lethal dose in animals (LC_{50} = 700 ppm) has caused marked congestion of the internal organs and slight congestion of the brain. Lungs also showed emphysema (Ref. 1).

Nitrobenzene

Nitrobenzene is a suspected carcinogen (Ref. 6). When administered to pregnant rats, it caused abnormalities in some of the fetuses examined (Ref. 10). Changes were observed in the chorionic and placental tissues of pregnant workers exposed to nitrobenzene (Ref. 6), and menstrual disturbances after chronic exposure have been reported. Chronic exposure to nitrobenzene has been found to cause a variety of blood disorders. Nitrobenzene is toxic in varying degrees to several salt- and fresh-water organisms (Ref. 1,34).

Pyridine

Pyridine exhibits moderate toxicity when absorbed into the human body through oral, dermal, and inhalation routes (Ref. 39). Liver and kidney damage have been produced in animals and man after oral administration (Ref. 5). In small doses, conjunctivitis, dizziness, vomiting, diarrhea, and jaundice may appear; tremors and ataxia, irritation of the respiratory tract with asthmatic breathing, and paralysis of eye muscles, vocal cords and bladder also have been reported (Ref. 39). Adverse taste in fish (carp, rudd) has been reported at five ppm. Pyridine causes inhibition of cell multiplication in algae and bacteria at 28 and 340 ppm, respectively (Ref. 1,40).

Tetrachloroethylene

Tetrachloroethylene was reported to be carcinogenic to mice (Ref. 18). A National Institutes of Health study (Ref. 43) has indicated that tetrachloroethylene, when administered orally, is carcinogenic to male F344/N rats and both sexes of B6C3F1 mice. Tetrachloroethylene is chronically toxic to rats and mice, causing kidney and liver damage (Ref. 11,18,42); and to humans, causing impaired liver function (Ref. 4). Additionally, tetrachloroethylene is slightly toxic to freshwater fish. Subjective central nervous system complaints were noted in workers occupationally exposed to tetrachloroethylene (Ref. 14). Tetrachloroethylene exposure is reported to cause alcohol intolerance in humans.

Carbon Tetrachloride

Carbon tetrachloride has been included on EPA's list of chemicals which have demonstrated substantial evidence of carcinogenicity (Ref. 33). In addition, toxicological data for non-human mammals are extensive and show carbon tetrachloride to cause liver and kidney damage, biochemical changes in liver function, and neurological damage (Ref. 36).

Toluene

Toluene is a toxic chemical that can be absorbed into the body by inhalation, ingestion, and through the skin. Data on its mutagenicity and carcinogenicity are inconclusive, but it has been reported to cause chromosomal change; teratogenic problems were also recently reported (Ref. 21). The acute toxic effect is central nervous system depression (Ref. 35), and irritation of eye and throat. These effects occur at low concentrations (200 ppm) (Ref. 22). Chronic occupational exposure to toluene has led to the development of neuro-muscular disorders. Occupational exposure of female workers to toluene has been reported to cause several reproductive problems, both to the woman and the offspring (Ref. 27). Chronic toluene exposure can cause dermatitis, affect the immune system, and cause permanent damage to the central nervous system (Ref. 3). Since toluene is metabolized in the body by a protective enzyme system which is also involved in the elimination of other toxins, it appears that over-loading the metabolic pathways with toluene may greatly reduce the clearance of other more

toxic chemicals. Additionally, the high affinity of toluene for fatty tissue can assist in the absorption of other toxic chemicals into the body. Thus, synergistic effects of toluene on the toxicities of other contaminants may render the waste stream more hazardous (Ref. 1).

1,1,1-Trichloroethane

Data regarding the carcinogenicity of 1,1,1-trichloroethane are inconclusive. (Ref. 19). It is mutagenic in the Ames test and in a mamallian cell transformation system (Ref. 1). Chronic exposure, albeit at greater than ambient levels, can cause central nervous system disorders in humans. Animal studies showed toxic effects on the central nervous system, cardiovascular system, and pulmonary system, and induced liver and kidney damage (Ref. 29).

Trichloroethylene

Trichloroethylene has been reported to be carcinogenic to mice (Ref. 17). It has also been identified by the Agency as a chemical which has demonstrated substantial evidence of being carcinogenic (Ref. 33). Industrial exposure to trichloroethylene caused some cases of central nervous system disturbances (headaches, insomnia, tremors) as well as peripheral nervous system impairment (neuritis, temporary loss of tactile sense, finger paralysis) (Ref. 2,13). Rare cases of hepatic damage have been reported following repeated abuse of trichloroethylene (Ref. 8). Trichloroethylene was found to be toxic in varying degrees to several freshwater organisms (Ref. 32). There was also a 50 percent decrease noted in ^{14}C uptake by a saltwater algae at a concentration of 8,000 mg/l (Ref. 1,23).

Trichlorofluoromethane

The Agency's primary concern in originally listing this solvent was the air pollution hazard resulting from its release at the surface of the earth. This can have many adverse health and environmental effects including skin cancer resulting from the depletion of the stratospheric ozone (Ref. 15,16). However, additional adverse health effects have also been found. Exposure of rabbits to trichlorofluoromethane was reported to cause cardiac arrhythmias (Ref. 30). It

induced cardiac arrhythmias, sensitized the heart to epinephrine-induced arrhythmias, and caused tachycardia (increased heart rate), myocardial depression, and hypertension in the monkey, dog, rat, and mouse (Ref. 30).

1,1,2-Trichloro-1,2,2-trifluoroethane

The Agency's primary concern in originally listing this solvent was the air pollution hazard resulting from its release at the surface of the earth. This can have many adverse health and environmental effects including increased incidence of skin cancer, reduced productivity in several important agricultural crops, and increased mortality in the larval forms of several important seafood species resulting from the depletion of the stratospheric ozone (Ref. 15,16).

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SECTION V

DAMAGE INCIDENTS

Both air and water pollution can occur from the land disposal of solvent wastes. In particular, volatilization and leakage into soil, groundwater, and surface water are mechanisms by which solvents enter the environment. This section describes incidents in which environmental contamination has occurred due to volatilization or migration of solvents.

Volatilization of Solvents from Land Disposal Sites

Many solvents are highly volatile and therefore are likely to escape into the atmosphere. Release of these toxic solvents to the atmosphere may pose adverse effects to humans and animals.

The major route for contaminant escape from California Class I landfills (which may accept hazardous wastes) is believed to be to the atmosphere (see Table V-1). Seven of the nine California Class I landfills have been the site of either explosions, vapor clouds, or ongoing air contamination. The California Air Resources Board (ARB) estimates that over 370,000 tons per year of volatile organic wastes are disposed at Class I landfill sites (Ref. 1 as presented in Ref. 6).

The California Air Resources Board conducted a study designed to measure the escape of volatile organics from land disposal areas. The study showed that high levels of hydrocarbons were being emitted from major hazardous waste disposal sites. In some cases the hydrocarbon levels detected were several orders of magnitude higher than the National Ambient Air Quality Standard for hydrocarbon emissions. From the results of the study, ARB concluded that current land disposal practices do not adequately prevent the air emissions of certain organic compounds, but instead allow substantial emissions of these compounds to the environment (Ref. 2).

The emissions of hydrocarbons were monitored at five California Class I sites from November 1979 to December 1979. Data on three of the sites are available. The study showed that in overall total carbon loading, the downwind levels were

TABLE V-1. PERFORMANCE OF CALIFORNIA CLASS I LANDFILLS

Site	Years of Operation	Type of Activity	History	References*
BKK (LA County)	1975 -	Codisposal	Measured air contamination (incl. benzene, vinyl chloride, chloroform, carbon tetrachloride)	2, 3, 4, 5 (#22)
Big Blue Hills (Fresno County)	1974 -	Landfill 4 wks/yr	Explosion/fire	4, 5 (#12)
Casmalia (Santa Barbara Co.)	1976 -	Landfill, Landspreading, Ponds		
Kettleman Hills (Kings County)	1976 -	Landfill, Landspreading, Ponds	Measured air contamination (incl. benzene)	2, 3
Richmond (Contra Costa County)	1964 -	Pond, Landfill	Groundwater contamination by metals & organics; vapor escape; rains caused pond overflow	5 (#6, #20)
Closed				
Calabasas (LA County)	1965 - 80	Codisposal	Vapor escape, leachate migration (thought to be due to improper siting)	5 (#7, #22)
Otay (San Diego County)	- 80	Landfill	Vapor escape	5 (#19)
Palos Verdes (LA County)	- 80	Landfill	Vapor escape, benzene found in ambient air	3,5 (#22)
Simi Valley (Ventura Co.)	1971 - 80	Landfill, Landspreading	Groundwater contamination by organics	5 (#8)

* References with "#" indicate case studies in Reference 5.

Source: References in table as presented in Reference 6.

1100 percent higher than the upwind levels at two of the sites and the downwind levels were 160 percent higher than the upwind levels at one of the sites. Levels of hydrocarbons detected at these three sites are shown in Table V-2. Additional monitoring was conducted at Site A. The results are presented in Table V-3.

Contamination of Soil and Groundwater

Solvent contamination of soil and groundwater has occurred at several land disposal sites. In Wilsonville, Illinois, a secure landfill lined with five feet of recompacted natural clay was found to be leaking (Ref. 8). Concentrations of halogenated organics as high as 36 percent were found in monitoring wells nine feet from the site (Ref. 8). In addition, a study conducted in eleven states showed that 43 out of 50 industrial waste land disposal sites have contaminated groundwater. In many cases chlorinated solvents were found in this groundwater.

The Class I landfills in California also present a surface waste and groundwater problem. During periods of heavy rain the evaporation ponds have overflowed, and thus released a contaminant discharge (Ref. 5). To date, groundwater contamination has been found at three of the nine California Class I landfills (see Table V-1).

Performance results for four of the five licensed secure landfills in New Jersey also have been analyzed (Ref. 10, 11). Each of the sites is constructed with a primary clay or synthetic liner, a leak detection/collection system, a secondary clay or synthetic liner, and a groundwater monitoring system. The landfills are owned and operated by private companies.

In all four cases, there is evidence of leakage of solvents from chemical wastes through the primary liner within the first two years of operation (see Table V-4). Performance of the secondary liners is unknown at this time, possibly owing to the time required for groundwater movement to reach the monitoring wells. In addition, analysis for contaminants originating in these landfills is hindered because the groundwater is already contaminated by previous landfill operations. Moreover, "developing a groundwater monitoring network that can distinguish one landfills' pollution from the pollution of neighboring industries is neither simple nor easy" (Ref. 11).

Table V-2. SUMMARY OF ANALYTICAL DATA, OSWEGO, NY SITE

Compound	1980 Data (ppm)		1984 Data (ppb)	
	Surface water	Ground-water	Surface water	Ground-water
Benzene				5,500
Chlorobenzene			51	480
1,2-Dichloroethane				3,500
1,1,1-Trichloroethane		685	51	560
Chloroform				290
1,2-Transdichloroethylene				5,300
Ethylbenzene				5,000
Methylene Chloride	7.12	265	24,000	120,000
Toluene	4.63	37.2	4,300	16,000
Trichloroethylene		13.2	290	15,000
Xylenes				36,000
Tetrachloroethylene			290	
1,1,2-Trichloroethane			7.1	
o-Dichlorobenzene			33	160

Source: Reference 17 (1980 data) and Reference 18 (1984 data).

TABLE V-3. MAXIMUM MEASURED HYDROCARBON CONCENTRATIONS AT SITE A

Hydrocarbon	Concentration (ug/m^3)
Acetone	120.0
Carbon Disulfide	11.0
Chloroform	190.0
Carbon Tetrachloride	9.9
Methylene Chloride	410.0
Ethyl Benzene	950.0
Ethyl Ether	36.0
Methyl Ethyl Ketone	15.8
Tetrachloroethylene	234.0
1,1,1-Trichloroethane	79.0
1,1,2-Trichloroethane	77.0
Toluene	2,400.0
Xylene	3,580.0

Source: Reference 2

TABLE V-4. PERFORMANCE DATA FOR FOUR NEW JERSEY SECURE LANDFILLS

Site	Year Opened	Primary Liner Material	Leak Discovered*	Secondary Liner Material
Glouchester County	1978	18" clay	1979	12" clay**
Deepwater	1979	30-mil nylon reinforced Hypalon	1979	30-mil nylon reinforced Hypalon
Phillipsburg	1979	30-mil PVC	1981	30-mil PVC
Ocean County	1978	30-mil PVC	1979	20-mil PVC

* The method of discovery involved statistical interpretation of results of laboratory analysis of liquids collected in the layer between the primary and secondary liners.

** There was some evidence of groundwater contamination in 1980, though interpretation of the monitoring data is controversial.

Source: References 10 and 11 as presented in Reference 6.

In addition to environmental contamination due to solvent leakage from lined facilities, incidents of solvent contamination from unlined facilities also have been documented. These incidents are much more numerous than those involving lined facilities, and they represent "worst-case" situations. Following are descriptions of several of these incidents.

A liquid waste incineration facility near Oswego, New York had toxic, flammable, and explosive wastes remaining at the site in drums, lagoons, and tanks after the facility was closed by the state. The wastes included off-specification polymer gels, plating wastes, metals sludges, paint wastes, and laboratory chemicals (Ref. 9). The aquifer beneath the site is used for drinking water, and families in the area that had private wells have changed to city water because of groundwater contamination (Ref. 17). Contaminants detected in the air at the site include toluene, ethyl benzene, xylenes, 1,1,1-trichloroethane, carbon tetrachloride, trichloroethylene, and tetrachloroethylene (Ref. 17). Levels of volatile compounds detected in surface water and groundwater are shown in Table V-5. It is not known specifically which surface water and groundwater contaminants came from the lagoons and which came from the tanks and drums. However, it is generally assumed that contamination of both surface water and groundwater is due in part to leakage and overflow from the lagoons (Ref. 20).

In Freehold, New Jersey a 45-acre landfill has received municipal refuse, septage wastes, drummed waste, and several million gallons of bulk liquid chemical wastes, the nature of which is largely unknown (Ref. 9). It is alleged that 50,000 drums of waste were disposed at the site over a three-year period, and that the bulk liquid wastes include two million gallons of toluene and spent solvents (Ref. 17). Six thousand people have been affected by contaminated groundwater downstream from the site (Ref. 17). Volatile organics detected in the groundwater at the site are shown in Table V-6. No contamination has been detected in groundwater upstream from the site (Ref. 17), indicating that background concentrations of the contaminants before leakage of the disposal facility were non-existent.

Three sites in Pennsylvania also show surface water and/or groundwater contamination from land disposal of solvent wastes. The groundwater under a landfill site in Union Township is contaminated by various inorganic and organic pollutants, including trichloroethylene and tetrachloroethylene. The aquifer is

TABLE V-5. SUMMARY OF ANALYTICAL DATA, OSWEGO, NY SITE

Compound	1980 Data (ppm)		1984 Data (ppb)	
	Surface water	Ground-water	Surface water	Ground-water
Benzene				5,500
Chlorobenzene			51	480
1,2-Dichloroethane				3,500
1,1,1-Trichloroethane		685	51	560
Chloroform				290
1,2-Transdichloroethylene				5,300
Ethylbenzene				5,000
Methylene Chloride	7.12	265	24,000	120,000
Toluene	4.63	37.2	4,300	16,000
Trichloroethylene		13.2	290	15,000
Xylenes				36,000
Tetrachloroethylene			290	
1,1,2-Trichloroethane			7.1	
o-Dichlorobenzene			33	160

Source: Reference 17 (1980 data) and Reference 18 (1984 data).

TABLE V-6. SUMMARY OF GROUNDWATER ANALYTICAL DATA, FREEHOLD, NJ SITE

Compound	Maximum Detected Concentration (ppb)
Benzene	1,939
Chlorobenzene	97
1,2-Dichloroethane	1,655
1,1-Dichloroethane	208
1,2-trans-Dichloroethylene	2,128
Ethylbenzene	3,325
Methylene Chloride	527
Tetrachloroethylene	76
Toluene	4,708
Trichloroethylene	1,423
Vinyl Chloride	334

Source: Reference 19

used as a source of drinking water by 1700 people within three miles of the site (Ref. 12). From 1947 to the present chlorinated organic solvents have been landfilled and landspread at a facility in Franklin County. The groundwater beneath the area and surface waters draining from the area are contaminated with chlorinated organic chemicals, including chloroform, 1,1-dichloroethylene, 1,1,1-trichloroethane, and trichloroethylene (Ref. 12). The third Pennsylvania site is a landfill in Hopewell Township that had received 400 tons of municipal and industrial waste per day. The off-site groundwater is contaminated with several organic chemcials, including tetrachloroethylene, 1,1,1-trichlorethane, 1,1-dichloroethane, and methyl ethyl ketone. There are 2220 people within three miles of the site that use the aquifer for drinking water, and 26 homes are currently being provided with bottled water because their wells are contaminated (Ref. 12).

In Glouchester, Rhode Island, a landfill in operation between 1974 and 1976 was permitted by the state to accept municipal wastes but is now showing both surface water and groundwater contamination that has been confirmed by EPA. The contaminants include toluene, chloroform, benzene, 1,1-dichloroethane, and 1,1,1-trichloroethane. There are 3800 people within three miles of the site who use the groundwater for drinking purposes (Ref. 12).

In one incident in Michigan, an automotive parts manufacturing plant routinely dumped spent degreasing solutions on the open ground at a rate of about 1000 gallons per year from 1968 to 1972. Trichloroethylene was one of the degreasing solvents present in the spent solutions. Beginning in 1973, trichloroethylene was detected at levels up to 20 mg/l in nearby residential wells. The dump site was the only apparent source of the contamination (Ref. 13).

In April 1974, a private water well in Bay City, Michigan became contaminated by trichloroethylene. The only nearby source of this chemical was a company which claimed that, although it had discharged trichloroethylene into the ground in the past, it had not done so since 1968. Nevertheless, in May 1975, two more wells were reported to be contaminated with trichloroethylene at concentrations of 20 mg/l and 3 mg/l, respectively (Ref. 14).

In another instance in Michigan, trichloroethylene was dumped on the ground and later found to have migrated into groundwater. The trichloroethylene, which had been dumped at a rate of 1000 gallons per year over a four-year period, was

detected in residential wells as far as 1100 feet from the site of dumping. Concentrations ranged as high as 28 ppm (Ref. 14).

A sump overflow in 1971 allowed trichloroethylene wastes to leak into a cooling pond. Seepage from this pond was found to contaminate a private well 75 yards distant and a company well at the site (Ref. 14).

Open dumping of wastes, including solvent wastes, from a chemical packing plant resulted in entry of organic solvents into the water table and contamination of several nearby water wells in 1973. One family reported illness resulting from use of the contaminated well water (Ref. 14).

The 4.5-acre Shope Landfill site in Girard, Pennsylvania had scrap rubber, paper, wooden pallets, cement, oils, solvents, acids, and caustics dumped on the site from the late 1950s until the 1970s. A total of 37 individual wells (in 15 clusters) was drilled and groundwater contamination from landfill leachate was been detected, as shown by the data in Table V-7. The contaminated groundwater plume, including the area under the landfill, covers eight acres (Ref. 15).

Near Atlantic City, New Jersey is an inactive landfill site known as Price Landfill. It operated from the mid-1960s to the mid-1970s, prior to which time it was a sand and gravel pit. The sand and gravel operation was terminated when it had been excavated to within about two feet of the groundwater level, and the facility then began receiving wastes from municipal and private sources. For approximately 18 months, the facility received drummed and bulk liquid industrial wastes. When landfill operations ended in the mid-1970s, the facility was covered with sand and gravel. The site is underlain by two major aquifers, both of which are used as public and private drinking water supplies. The upper aquifer contains a contaminant plume of pollutants such as benzene, 1,2-dichloroethane, toluene, vinyl chloride, phenol, bis (2-ethylhexyl) phthalate, and several heavy metals. There is strong evidence that the plume is moving toward the wellfield that supplies drinking water to Atlantic City (Ref. 16).

TABLE V-7. LEACHATE ANALYTICAL DATA, GIRARD, PA SITE

Compound	Average Concentration in Leachate (mg/l)	Mass Loading (lb/day)
acetone	1,131	0.038
methyl ethyl ketone	386	0.013
methyl isobutyl ketone	13,980	0.46
toluene	1,313	0.044
xylene	2,340	0.078
1,2-dichloroethylene	893	0.030
1,1-dichloroethylene	18,852	0.63
total volatile organics	129,000	4.3
total halogenated volatile organics	89,900	3.0

Source: Reference 7

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